

# CHEMICAL DERIVATIVES OF FATS FOR INDUSTRIAL UTILISATION

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**D**URING the economic depression of the early 1930's, farmers in the United States experienced limited markets for their commodities at disastrously low prices. This situation led to the Congressional Act of 1938 which provided for the establishment of a utilisation research programme for agricultural commodities. Four large laboratories were built, each capable of accommodating about 200 scientists and their supporting staff. Actual research was initiated during the summer of 1940.

The objective of the utilisation research programme in the four laboratories is the development of new and improved food, feed and industrial outlets for farm commodities. The programme is divided among the four laboratories primarily on a commodity basis. In general, those commodities having a special regional interest are assigned to the laboratory in the area. Thus corn, soya beans, and flaxseed, which are products of our Midwest, are worked on most extensively by the Northern laboratory, whereas cotton and peanuts receive the special attention of our Southern Division. In the assignment of commodities having less specific regional characteristics, animal fat research was assigned to the Eastern Laboratory which is located in suburban Philadelphia.

In consideration of the fields in which increased or new outlets for animal fats may be found, the constancy of the *per capita* consumption of food fats and oils in the United States is an important and directive fact. Except under rationing during World War II, the annual *per capita* disappearance of food fats and oils has been remarkably uniform at 44-46 lb./yr. (20-21 kilo/yr.) for over 30 years. It must be concluded that aside from increased consumption due to population growth, enlarged domestic outlets for fats and oils will probably lie almost entirely in the industrial field. This is especially true of the animal fats which are produced under conditions which lead to about half of our total output being classified as inedible. Therefore about 75% of our research programme has been directed toward industrial utilisation.

## Research Programme and Accomplishments

*Edible animal fats (lard and tallow).*—Lard production alone averages nearly 2.8 billion lb. a year and edible tallow production has averaged about 100 million lb. a year. Our research programme was initiated after the edible animal fats had fallen into disfavour with the American housewife. Therefore,

all factors affecting the quality and acceptance of these fats deserved careful consideration. The properties of particular significance appeared to be keeping quality or stability, physical characteristics—such as plastic range, consistency and the creaming power, odour, flavour, colour and smoke point.

It was soon apparent that increased stability was a fundamental need of the edible animal fats. Without it the improvement in other respects could have little value, because the best shortening is unfit for use if it is rancid. Therefore, our early work was directed to a study of methods for measuring and increasing stability in bulk fats.

As a result of our studies in the field a convenient method for improving the shelf life of home-rendered lard was devised.<sup>1</sup> This method which involved the addition of a vegetable oil or hydrogenated vegetable oil to the home-rendered lard was convenient to use on the farm. We were also the first to achieve a practical synthesis of the long-chain alkyl gallates and report on their activity as antioxidants.<sup>2,3</sup> These compounds have been investigated more extensively on the Continent where they enjoy some use as fat additives.

Contributions have also been made to the mechanism of antioxidant action and to the role of the synergists. Studies have also been made on both the fatty acid composition and on the component glycerides of lard and tallow as well as on methods for study of glyceride structure. Particularly noteworthy has been the development of an infrared method for quantitative determination of trans-double bonds.<sup>4</sup>

These studies have played a part in the increased use of edible animal fats in the manufacture of shortenings. Data showing the change taking place in the United States in this respect are shown in the Table.

Table  
Use of animal fats in shortenings in the United States

	Edible Tallow	Lard	Oleostearine and Oleo Oil
	(Million lb.)		
1950	17	155	14
1954	81	142	8
1955	111	334	7
1956	135	459	5
1957	220	376	6
1958	248*	425*	4*

\* Preliminary figures, fats and oils situation. U.S. Department of Agriculture.

A problem of prime importance to all segments of the livestock industry is the possible relationships between atherosclerosis and the amount and nature of dietary fat. From a conviction that greater understanding of this field requires vastly improved methodology, the present efforts of the research group assigned to edible fats are largely directed to development of improved analytical tools for use in fat analysis. Particular attention is being given to spectroscopy and chromatography.

**Inedible animal fats.**—The production of inedible animal fats in the United States is currently about 3 billion lb. or 1,300,000 metric tons per year. Tonnage produced has increased by about 50% during the past decade while the principal outlet in the soap-kettle was diminishing by about the same percentage.

Even 20 years ago, it seemed logical to suppose that the animal fats *per se* as well as fractions readily obtained from them had been evaluated for most industrial uses then current and that their unique properties and characteristics were being utilised about as fully as possible. It therefore seemed probable that, aside from use in feeds, development of new uses would be dependent upon their chemical modification to materials having new and more useful characteristics. A precedent for this approach is found in the petrochemical industry.

Chemical modification, therefore, to produce "oleochemicals" seemed one of the more promising routes to increased utilisation, but the mere synthesis of new compounds holds no special promise; it is essential that the modification be directed. Fortunately the long, straight-chain structures of the fatty acids from animal fats frequently offer advantages and seldom pose serious disadvantages in such fields as plastics, rubber, synthetic fibres, surface-active agents, plasticisers, lubricants and waxes. It is exceedingly fortunate for those interested in the use of inedible fats that the fields in which the basic chemical composition of fatty acids appears to give them certain advantages coincide to a considerable extent with the major fields of use for organic chemicals.

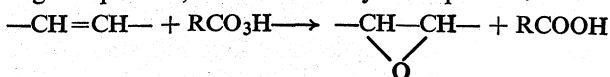
Experience indicates that if the fatty acids are to be used as chemical intermediates, it will be advantageous to have them available in commercially pure forms.

**Oleic acid.**—Commercial progress in the use of fractional distillation and fractional crystallisation from solvents has permitted the production and marketing of relatively pure saturated fatty acids for quite some time. The first process proposed for the commercial preparation of a purified monoethenoic acid (oleic), however, came from our laboratory (Swern, *et al.*).<sup>5</sup> The desired results were obtained by alteration of the poly-unsaturated acids in tallow or grease by selective hydrogenation followed by separation of the saturated acids either by crystallisation or pressing methods. The unsaturated acids resulting from such treatment are essentially monoethenoic in nature. A modification of this approach to the preparation of commercially pure oleic acid has been described by Goebel.<sup>6</sup> He reduced the content of poly-unsaturated components to very low levels by their selective polymerisation in the presence of steam,

which serves to minimise decarboxylation. Finally it should be noted that in the United States at least one commercial producer of oleic acid has approached the goal through the use of raw material selection.

**Oxygenated derivatives.**—In the study of derivatives having practical value the oxidation of unsaturated fatty acids in various ways has been the most important project with which we have been concerned. Oxidation by means of air or oxygen has been extensively studied. These studies have contributed to our understanding of the mechanism of these reactions, but they showed that the products were too complex a mixture for the reaction to have practical synthetic value.

Of the various methods for chemical oxidation our work on epoxidation has had the greatest practical results. Epoxidation is the conversion of an olefinic double bond to the oxirane group by reaction with an organic peracid, as illustrated by the equation:



The reaction was discovered by the Russian chemist, Prileschajew<sup>7</sup> who showed that perbenzoic acid is an efficient epoxidising agent. The application of this reaction to fats, oils and fatty derivatives received the special attention of Swern and co-workers at our laboratory.<sup>8</sup> These workers studied the epoxidation not only of natural fats, but also of a wide variety of fatty derivatives using peracetic acid prepared *in situ* by the action of hydrogen peroxide.

The introduction of the oxirane group into the alkyl chain of a fatty ester markedly increases its compatibility with polyvinyl chloride and other resinous materials. Furthermore, the oxirane group exerts a marked stabilising effect on chlorine-containing polymers. These desirable characteristics have resulted in the commercial use of epoxidised fatty acid esters as stabilising-plasticisers for chlorine-containing polymers and copolymers. Other acid-scavenging applications are also reported from time to time.

Numerous epoxy esters simpler than the triglycerides have also been reported. In general these have excellent compatibility with polyvinyl chloride and at the same time impart improved low temperature characteristics to the polymer. It is not to be concluded, however, that outlets for epoxidised oils such as soya bean oil are decreasing. In fact, recent work describing their use as polyols indicates they may have a period of further expanding use.

**Monohydroxy acids.**—Several methods for the preparation of monohydroxy acids from oleic acids have been explored.

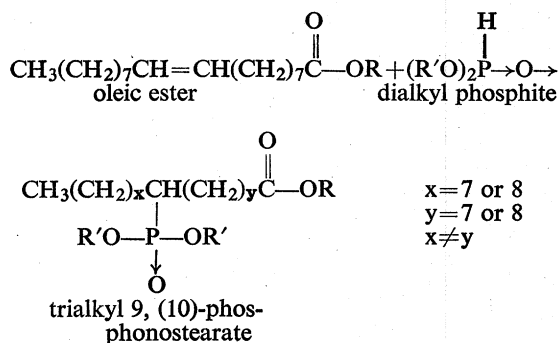
A mixture of isomeric monohydroxystearic acid is obtained in good yield from oleic acid by the low temperature reaction with concentrated sulphuric acid followed by hydrolysis of the intermediate sulphate esters.<sup>9</sup>

Another convenient procedure for preparing monohydroxystearic acids of known structure is hydrogenation of the corresponding oxirane. No more than two isomeric monohydroxystearic acids are apparently obtained, and evidence indicates that the isomer

which predominates is the one in which the hydroxyl group is farther from the carboxyl group.<sup>10</sup>

An interesting reaction reported in 1953 from our laboratory<sup>11</sup> for the synthesis of monohydroxy acids is the addition of 90–100% formic acid at its boiling point to olefinic acids, followed by hydrolysis of the intermediate formate esters. The reaction rate is increased considerably by acidic catalysts, particularly perchloric and sulphuric acids and boron fluoride. The yield of monohydroxystearic acids from oleic acid is over 70% with the 9- and 10-isomers predominating.

**Phosphorus derivatives.**—During the past few years a number of phosphorus derivatives of fatty acids has been prepared in our laboratory. One of the most interesting reactions involving phosphorus derivatives of fatty acids is described in our recent report<sup>12</sup> that such phosphonates as the dimethyl, diethyl, di-n-butyl and di-2-ethylhexyl phosphites can be added not only to terminal double bonds (undecenoates, vinyl esters) but also to non-terminal double bonds (oleate). Conditions required include presence of a free radical catalyst such as a decomposing peroxide. Thus trialkyl 9(10)-phosphonostearates were prepared in 66–77% yield by adding dialkyl phosphonates to alkyl oleates in the presence of decomposing t-butyl perbenzoate.

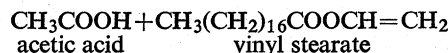
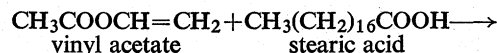


Some of these phosphorus-containing fatty acid derivatives show characteristics indicative of potential value as plasticisers and as lubricant additives.

**$\alpha$ -Sulphonates.**—Chain-substituted derivatives of fatty acids can also be prepared from saturated acids by substitution reactions. Although sulphonation of saturated acids was described previously, only recently has an efficient preparative reaction been described and unequivocal proof offered<sup>13</sup> that sulphonation takes place exclusively in the  $\alpha$ -position to the carboxyl group. Long chain fatty acids in tetrachloroethylene can be  $\alpha$ -sulphonated directly in high yield with liquid sulphur trioxide. Numerous salts of the  $\alpha$ -sulphonated fatty acids and of their esters have been made and characterised. Uses for these materials related to their surface active character are being studied.

**Carboxyl group reactions.**—Considerably less attention has been given to reactions of the carboxyl group than to chain reactions. One important area of activity must be noted however. This is the field of

vinyl esters and ethers. Reppe<sup>14</sup> reported preparation of the vinyl esters of a number of the commercially important fatty acids by direct vinylation with acetylene. Possibly because his products lacked chemical and functional purity, however, they did not receive favourable attention. We explored the preparation of vinyl esters using the acidolysis technique.<sup>15</sup>



The homopolymerisation of vinyl stearate and its copolymerisation with other monomers such as vinyl acetate and vinyl chloride have also been studied extensively. In general, its use as a co-monomer has given products having increased moisture resistance and increased flexibility when compared with the unmodified polymers.

**Miscellaneous.**—Many other potentially important reactions have been studied. Some further reactions which illustrate the variety of the studies we have made are noted briefly.

The oxidation of oleic acid with neutral, dilute aqueous potassium permanganate produces 9(10), 10(9)-hydroxyketostearic acids. Yields reported, however, have been poor, probably seldom exceeding 30% and often much lower. Recent work in our laboratory<sup>16</sup> has shown that 65–75% conversion of oleic acid to ketohydroxystearic acids can be obtained. Ketohydroxystearic acids are of interest because they may be easily reduced, oxidised and cleaved.

Dihydroxy acids with non-adjacent hydroxyl groups are not well known but some study has been devoted to their preparation. Reaction of formic acid with linoleic acid leads to a good yield of a mixture of approximately equal parts of dihydroxystearic and monohydroxyoctadecenoic acid.<sup>17</sup>

Workers in our laboratory have also prepared a variety of sulphur-containing derivatives of fatty acids. These include 9(10)-(carbomethylthio)-stearic acid prepared by the addition of mercaptoacetic acid to oleic acid under free radical conditions and the 9(10)-(acetylthio)-stearates which are prepared by addition of thiolacetic acid to methyl oleate.

## Conclusion

The production of both edible and inedible animal fats in the United States has increased substantially during the past decade while the usual outlets have dwindled. The edible animal fats are finding increased outlet as shortenings. Most of our research programme, however, is directed to the preparation of fat derivatives and to their evaluation of the latter for use in industrial fields in which their unique chemical structure offers advantages. In this way markets in such diversified areas as plasticisers, plastics, surface active agents and waxes are being found.

# References

- <sup>1</sup> Riemenschneider, R. W., Ault, W. C. & Wells, P. A., AIC-157, June, 1947
- <sup>2</sup> Ault, W. C., Weil, J. K., Nutting, G. C. & Cowan, J. C., *J. Amer. chem. Soc.*, 1947, **69**, 2003-2005
- <sup>3</sup> Morris, S. G., Krackel, L. A., Hammer, D., Myers, J. S. & Riemenschneider, R. W., *J. Amer. Oil Chemists' Soc.*, 1947, **24**, 309-311
- <sup>4</sup> Shreve, O. D., Heather, N. R., Knight, H. B. & Swern, D., *Anal. Chem.*, 1950, **22**, 1261-1263
- <sup>5</sup> Swern, D., Scanlan, J. T. & Roe, E. T., *Oil and Soap*, 1946, **23**, 128-131; Swern, D. & Ault, W. C., U.S. Patent 2,457,611
- <sup>6</sup> Goebel, C. G., *J. Amer. Oil Chemists' Soc.*, 1947, **24**, 65
- <sup>7</sup> Prileschajew, N., *Ber. dtsh. chem. Ges.*, 1909-1910, **42**, 4811; 1911, **43**, 609 and 1912, **44**, 613
- <sup>8</sup> Findley, T. W., Swern, D. & Scanlan, J. T., *J. Amer. chem. Soc.*, 1945, **67**, 412; Swern, D. & Findley, T. W., U.S. Patent 2,569,502
- <sup>9</sup> Roe, E. T., Schaeffer, B. B., Dixon, T. A. & Ault, W. C., *J. Amer. chem. Soc.*, 1944, **66**, 1924-1925; *J. Amer. Oil Chemists' Soc.*, 1947, **24**, 45-48
- <sup>10</sup> Mack, C. H. & Bickford, W. G., *J. org. Chem.*, 1953, **18**, 686
- <sup>11</sup> Knight, H. B., Koos, R. F. & Swern, D., *J. Amer. chem. Soc.*, 1953, **75**, 6212-6215; *J. Amer. Oil Chemists' Soc.*, 1954, **31**, 1-5
- <sup>12</sup> Sasin, R., Nauman, R. M. & Swern, D., *J. Amer. chem. Soc.*, 1959, **81**, 4335-4337; Sasin, R., Olszewski, W. F., Russell, J. R., & Swern, D., *J. Amer. chem. Soc.*, 1959, **81**, 6275-6277
- <sup>13</sup> Weil, J. K., Witnauer, L. P. & Stirton, A. J., *J. Amer. chem. Soc.*, 1953, **75**, 2526-2527
- <sup>14</sup> Reppe, Ger. Pat. 588,352; U.S. Pat. 2,066,075
- <sup>15</sup> Swern, D. & Jordan, E. F., Jr., *J. Amer. chem. Soc.*, 1948, **70**, 2334-2339
- <sup>16</sup> Coleman, J. E., Riciuti, C. & Swern, D., *J. Amer. chem. Soc.*, 1956, **78**, 5342-5345
- <sup>17</sup> Knight, H. B., Koos, R. E. & Swern, D., *J. Amer. chem. Soc.*, 1953, **75**, 6212-6215